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A Reconsideration of the Measurement of Polymer Interdiffusion by Fluorescence Nonradiative Energy Transfer

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ABSTRACT: A general formalism has been developed for quantitative determination of polymer self-diffusion coefficients, D_p, using fluorescence nonradiative energy transfer (NRET). The experimental geometry consists of a "sandwich" of two thin polymer films, one labeled with NRET donor chromophores and the other with NRET acceptor chromophores. D_p can be characterized self-consistently by steady-state fluorescence intensity measurements of donors or acceptors or by transient donor fluorescence intensity decay measurements as a function of interdiffusion time, t. For $t < x^2/(16D_p)$, where x is the thickness of the donor-labeled polymer layer, increases in the normalized acceptor intensity and normalized energy transfer efficiency with interdiffusion are the same and equal to $k_n(D_pt)^{1/2}/x$, where k_n is a function of the initial acceptor concentration. Similarly, the decrease in the normalized donor intensity with interdiffusion is proportional to $(D_pt)^{1/2}/x$. The general formalism presented here has been compared to earlier approaches, revealing that a previous method of analyzing the steady-state acceptor intensity in terms of polymer diffusion is merely a limiting case of the present formalism while a previous method of analyzing the donor intensity decays results in underestimates of D_p.

Introduction

Diffusion of macromolecules across polymer–polymer interfaces has been an active area of study for well over a decade.[1-19] Technologically, interest has arisen from issues related to polymer welding, crack healing, coextrusion, etc.[1-4,20-22] Experimentally, many of the techniques employed in measuring diffusion coefficients of polymers have involved the use of interfaces, either imposed on bulk samples through some photochemical or similar means[23-25] or by joining two distinct polymer films[5-18] and annealing at temperatures exceeding the glass transition temperature, T_g. Scientifically, by employing experimental systems involving interfaces, it may be possible to test many important issues ranging from determining the appropriate combination of dynamic and thermodynamic models[26-29] for describing mutual diffusion of either chemically identical polymers of different molecular weight (MW) or chemically different polymers to testing some of the basic tenets of reptation theory[15,30] using chemically identical polymers of like MW.

A major experimental hurdle has been associated with determining small diffusion coefficients (10^{-15} cm^2/s $< D < 10^{-20}$ cm^2/s) that may be associated with polymer self-diffusion or tracer or mutual diffusion. A number of techniques have overcome wholly or in part these limitations, among them small-angle neutron scattering (SANS),[10-12] forward recoil spectrometry (FRES),[5-8] dynamic secondary ion mass spectrometry (SIMS),[9] specular neutron reflection (SNR),[14,15] nuclear reaction analysis (NRA),[13] and spectroscopic ellipsometry.[16] In the case of interdiffusion of chemically identified polymers, spectroscopic ellipsometry is inapplicable, while SANS, FRES, SIMS, SNR, and NRA require a source of contrast, often accomplished through significant deuteration of the polymers in one of the two films. With this contrast provided, FRES, dynamic SIMS, and NRA can provide (via ex situ destructive testing) direct information on concentration profiles, important in the case of interdiffusion of polymers of different molecular weight but unnecessary in studying interdiffusion of polymers of like MW. SANS and SNR require that assumptions be made about composition profiles for polymers of unlike MW in order to fit data and determine diffusion coefficients.

A decade ago, a unique experimental approach for quantitatively monitoring the interdiffusion of chemically identical polymer chains of like MW across polymer–polymer interfaces without the use of extensive deuteration was described by Tirrell, Adolf, and Prager.[18,31] They proposed layering two thin polymer films, one with polymers lightly labeled with nonradiative energy-transfer (NRET) donor chromophores and the other with polymers lightly labeled with NRET acceptor chromophores. A typical distance for effective NRET interaction between donors and acceptors is on the order of 2 nm.[32] Thus, if a sample is illuminated with light preferentially absorbed by the donors, the initial acceptor fluorescence intensity, $I_A(0)$, will be due only to the small fraction of photons directly exciting the acceptors in the acceptor-rich film and any proximal pairs of acceptors and donors within 2 nm of the interface which are participating in NRET. As interdiffusion proceeds, the number of acceptors intermixed with donors increases, and an in situ study will reveal an increase in acceptor fluorescence intensity, $I_A(t)$, with annealing time. Tirrell, Adolf, and Prager indicated that the increase in $I_A(t)$ would obey the following equation:[18]

$$I_A(t) - I_A(0) = I_0\alpha \int_{-\infty}^{\infty} C_A(z,t)\, C_D(z,t)\, dz \qquad (1)$$

where I_0 is the incident light intensity, α is the proportionality factor which can be determined experimentally from the fluorescence of a homogeneous mixture of donor- and acceptor-labeled polymers, and C_A and C_D are the concentration profiles of the labeled polymers. Thus, by noting that the diffusion of chemically identical polymers of like MW is Fickian and measuring in situ the increase in $I_A(t)$ upon annealing, diffusion coefficients can be uniquely determined.

Given that the distance for effective NRET between donors and acceptors is on the order of 2 nm, it is likely

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that under optimal experimental circumstances the NRET technique can be sensitive to interdiffusion on a 1–5 nm distance scale. In contrast, SANS has a resolution limit of 10–30 nm,[10] dynamic SIMS 15 nm,[9] FRES 110 nm,[5] and SNR 0.5 nm.[14] While these latter techniques often require extensive deuteration of one film component to achieve contrast, NRET may require only simple end-labeling of the polymer chains with chromophores such as phenanthrene and anthracene. Furthermore, the NRET experiments proposed by Tirrell, Adolf, and Prager[18] require only a simple spectrofluorimeter which is generally much less expensive and much more readily available than the equipment used in the other experiments. In spite of these apparent advantages,[33,34] no direct quantitative, experimental test of the Tirrell–Adolf–Prager approach for studying polymer diffusion has yet been published. (Morawetz[35] has demonstrated that NRET is a very sensitive technique for investigating polymer chain dynamics, but the experiments were not designed to provide a quantitative analysis of diffusion.)

Over the past several years, Winnik and co-workers[19] have made significant progress in monitoring interdiffusion in latex polymer films by employing a different, ex situ, NRET approach involving transient donor intensity decay measurements. They have done extensive characterization of the diffusion of methacrylate-based polymers as a function of molecular weight, temperature, and the influence of plasticizers by modeling the transient donor intensity decay using the following equation:

$$I_{\mathrm{DN}}(t) = B_1 \exp(-\bar{t}/\tau_{\mathrm{d}} - 2\bar{\gamma}(\bar{t}/\tau_{\mathrm{d}})^{1/2}) + (1 - B_1) \exp(-\bar{t}/\tau_{\mathrm{d}}) \quad (2)$$

where $I_{\mathrm{DN}} = I_{\mathrm{D}}(\bar{t})/I_{\mathrm{D}}(0)$, B_1 is the fraction of those donors that can undergo energy transfer due to diffusive mixing, $1 - B_1$ corresponds to the fraction of donors that are not intermixed with acceptors, $\bar{t}$ is the excited-state decay measurement time, and τ_{d} is the excited-state lifetime of the donors in the absence of acceptors. (The origin of eq 2 and the definition of $\bar{\gamma}$ will be discussed in the next section.) Winnik and co-workers[19] use eq 2 to fit the donor intensity decay and thereby determine B_1 from which they calculate a diffusion coefficient. Recently, Boczar et al.[36] have also employed this approach to characterize interdiffusion between polymer latex particles. It is important to note that the concentration gradient of donors and acceptors in the mixed region is ignored in deriving eq 2.

Both the steady-state fluorescence intensity approach described by Tirrell, Adolf, and Prager[18] and the transient donor intensity decay characterization employed by Winnik and co-workers[19] provide ostensibly appealing ways for characterizing interdiffusion of polymers across interfaces. However, both have limitations. First, as formulated, both allow characterization only for the case of chemically identical polymers of like MW. Second, as is demonstrated later in this manuscript, the expression provided in eq 1 is valid in a limited range of low acceptor concentration. Finally, the expression provided in eq 2, which simplifies the analysis by ignoring the concentration gradient of donors and acceptors in the mixed regions, results in an underestimate of diffusion coefficients.

In the present work, a reconsideration of these NRET approaches has led to a general formalism which provides analytical solutions for the determination of the polymer self-diffusion coefficient, D_{p}, by steady-state fluorescence intensity and transient fluorescence intensity decay measurements. For time scales $t < x^2/(16D_{\mathrm{p}})$, where x is the thickness of the donor-labeled polymer film, the normalized steady-state acceptor fluorescence intensity, $I_{\mathrm{AN}}(t)$, is equal to $k_{\mathrm{n}}(D_{\mathrm{p}}t)^{1/2}/x$ where the factor k_{n} is a calculable function of the initial acceptor concentration. Similar exact expressions relating the energy-transfer efficiency, $E(t)$, to $(D_{\mathrm{p}}t)^{1/2}/x$ have also been derived for quantitative interpretation of transient donor intensity decay measurements in terms of diffusion coefficients. While the present manuscript is limited to the discussion of polymer self-diffusion, our ultimate goal is to provide theory for a relatively inexpensive means for quantitatively characterizing self-diffusion or tracer or mutual diffusion of polymers above T_{g} and tracer diffusion of small molecules in polymers[37] above and below T_{g} via photophysical techniques.

Review of NRET

In order to provide sufficient background for readers unfamiliar with the details of NRET to understand the basis of our approach, a brief review of NRET is warranted. (More extensive background may be obtained from refs 32 and 38–40.) When donor chromophores are excited using a narrow pulse of light, the excited donors return to the ground state either by emitting a photon of light (fluorescence) or through nonradiative mechanisms. For a well-behaved system consisting only of donor chromophores, after exposing the donors with a short pulse of light the fluorescence intensity decays exponentially with time. However, if acceptors are present in the vicinity of the excited donors, then there is a possibility of NRET from the excited donors to the ground-state acceptors.[38–40] The excited acceptor molecules, similar to the donors, can return to the ground state either by emitting a photon of light or through nonradiative mechanisms. It was shown by Förster[38,39] that the rate of transfer (probability of transfer per unit time, W_{NR}) depends on the inverse sixth power of the separation between the donors and the acceptors, R:

$$W_{\mathrm{NR}} = \frac{1}{\tau_{\mathrm{d}}}\left(\frac{R_{0\mathrm{AD}}}{R}\right)^6 \quad (3)$$

where $R_{0\mathrm{AD}}$ is the critical transfer distance determined by the overlap of the fluorescence spectrum of the excited donors and the absorption spectrum of acceptors.[32,38–40] Values of $R_{0\mathrm{AD}}$ range from roughly 1 to 4 nm.[32] The values of $R_{0\mathrm{AD}}$, greater than the atomic dimensions of the acceptors and donors, indicate that it is not necessary for the acceptors and donors to be in physical contact for NRET to take place.

The presence of NRET affects the fluorescence intensity decay of the donor molecules, which can be given by the following equation:[38,39,41]

$$I_{\mathrm{D}}(\bar{t}) = \frac{n_{\mathrm{D}}(0)}{\tau_{\mathrm{d}}}\int_0^\infty f(R) \exp\left(-\frac{\bar{t}}{\tau_{\mathrm{D}}} - \frac{\bar{t}}{\tau_{\mathrm{d}}}\left(\frac{R_{0\mathrm{AD}}}{R}\right)^6\right) \mathrm{d}R \quad (4)$$

where $n_{\mathrm{D}}(0)$ is the number of excited donors and $f(R)$ is the distribution of the distances between the donors and the acceptors. It is clear from eqs 3 and 4 that for $R = R_{0\mathrm{AD}}$ there is a fifty–fifty chance for an excited-state donor molecule to transfer the energy to a ground-state acceptor. As a consequence the apparent average donor excited-state lifetime is reduced by half. As the separation between the donors and the acceptors increases beyond $R_{0\mathrm{AD}}$, the contribution of NRET will drop off very rapidly. This sensitivity of NRET to the separation of the donors and acceptors has been used to measure end-to-end distance in oligomers,[42] to characterize phase separation in polymer blends,[43] and to study formation of micelles in block and graft polymers.[44]

For a three-dimensional system consisting of randomly distributed donors and acceptors, eq 4 can be written as[32,38,39,45]

$$I_D(\bar{t}) = \frac{n_D(0)}{\tau_d}\exp\left(-\frac{\bar{t}}{\tau_d} - 2\gamma\left(\frac{\bar{t}}{\tau_d}\right)^{1/2}\right) \qquad (5)$$

where $\gamma = C_A/A_0$, C_A is the concentration of acceptors in moles per liter, and A_0 can be written as[38]

$$A_0 = \frac{3000}{2\pi^{1.5}N_A R_{0AD}{}^3} \qquad (6)$$

where R_{0AD} has units of centimeters and N_A is Avagodro's number. The donor intensity decay in the presence of acceptors deviates strongly from the exponential decay expected for donors in the absence of acceptors. The magnitude of this deviation will depend on γ; when γ is 0.433, there will be a 50% probability of NRET. It is important to note that eqs 5 and 6 are valid in very viscous systems and in films where there is no significant change in the position of donor–acceptor pairs during the time the donor is in the excited state. It has been shown experimentally by Bennett[46] that eqs 5 and 6 give excellent fits for various donor–acceptor pairs doped in glassy polymeric films. His results also indicate that A_0, given by eq 6, is not a function of donor concentration from 10^{-4} to 10^{-2} mol/L.

Although eq 5 describes the donor intensity decay for donors and acceptors in viscous solution or films, it is not strictly correct if the donors and acceptors are covalently labeled to the polymer chain.[47] In that case, the distribution of acceptors relative to the donors is not entirely random but instead is correlated due to the higher probability of segments from the donor-labeled polymer being present near the donor. By introducing this nonrandomness in acceptor concentrations near the donors in Förster's analysis, Fredrickson[47] has shown that the donor lifetime can be expressed by eq 5 with an additional term due to screening. Mendelsohn et al.[48] have been investigating the significance of this additional contribution for various concentrations of acceptors and donors in end-labeled polymers. Their calculations indicate that often less than a 20% correction is incurred in the average lifetime predicted using eq 5 after taking into account the screening for end-labeled polymers. In this paper, we will use eq 5 as our building block to describe diffusion, and we will ignore the effects associated with correlations.

Results and Discussion

(A) Interdiffusion of Acceptor- and Donor-Labeled Polymers. In order to take advantage of the sensitivity of NRET to motion over small distances, we have developed a quantitative formalism using a sample geometry consisting of a "sandwich" of two thin polymer films layered on top of each other (see Figure 1), one labeled with donors and the other with acceptors. We neglect any non-Fickian effects which may be encountered at the earliest stages of the diffusion (present when chains have interdiffused approximately a radius of gyration or less across the interface)[2,3,15] and consider the diffusion mechanism to be Fickian[3] at all times.

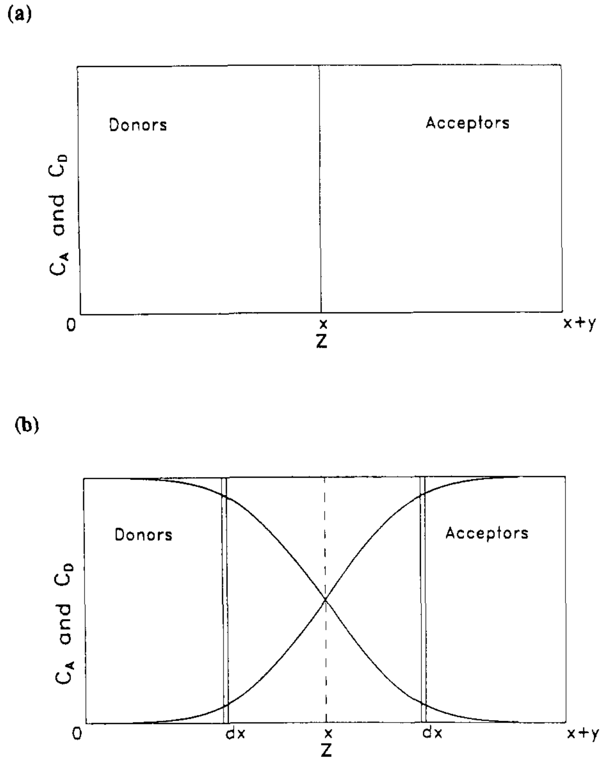

Figure 1. Concentration profile for donor- and acceptor-labeled polymers (a) before and (b) after diffusion.

When the sandwich sample in Figure 1 is heated to the measurement temperature above T_g, the donor- and acceptor-labeled polymers diffuse across the interface and the Fickian concentration profile of the donors can be written as follows:[49]

$$C_{DN}(z,t) = \frac{C_D(z,t)}{C_{D0}} = q\left\{1 + 2\sum_{n=1}^{n=\infty}\frac{\exp[-(\pi nq)^2\beta]\sin(\pi nq)\cos\left(\frac{\pi nqz}{x}\right)}{(\pi nq)}\right\} \qquad (7a)$$

where C_{D0} is the initial donor concentration before diffusion, $q = x/(x + y)$ and $\beta = D_pt/x^2$. (The thickness of the donor layer, x, is always considered to be less than or equal to that of the acceptor layer, y.) The acceptor concentration profile can be expressed as

$$\frac{C_A(z,t)}{C_{A0}} = \{1 - C_{DN}(z,t)\} \qquad (7b)$$

where C_{A0} is the initial acceptor concentration. For $t < x^2/(16D_p)$ eq 7a can be simplified to the well-known error function:[50]

$$C_{DN}(z,t) = \frac{1}{2}\left[1 - \mathrm{erf}\left(\frac{z - x}{2(D_pt)^{1/2}}\right)\right] \qquad (8)$$

Figure 1b shows typical Fickian donor and acceptor concentration profiles, with two narrow sections of thickness dx. In the section to the right (section 1) there are few donors surrounded by many acceptors, while in the section to the left (section 2) there are many donors but few acceptors. If we assume that both of these sections have an uncorrelated distribution of acceptors and donors, then we can easily see from eq 5 that the donors in section 1, where there are more acceptors, will decay from the excited state to the ground state much faster than the donors in section 2. Thus, to determine the donor intensity decay for the sample, we need to consider both $n_D(0)$ and γ, in eq 5, to be functions of position. The decay of the donor fluorescence intensity for the entire sample can be written as an integration over infinitesimally narrow individual sections:

$$I_{\mathrm{DN}}(\bar{t},t) = \frac{I_{\mathrm{D}}(\bar{t},t)}{I_0} = \frac{1}{x}\int_0^{x+y} C_{\mathrm{DN}}(z,t) \times \exp\left(-\left(\frac{\bar{t}}{\tau_{\mathrm{d}}}\right) - 2\gamma(z,t)\left(\frac{\bar{t}}{\tau_{\mathrm{d}}}\right)^{1/2}\right)\mathrm{d}z \quad (9)$$

where $\gamma = C_{\mathrm{A}}(z,t)/A_0$ and I_0 is the donor intensity at $\bar{t} = 0$. It is important to distinguish the two time variables in eq 9, one the diffusion time, t, on the order of minutes to months and the other the time scale during which the excited donor chromophores return to the ground state, $\bar{t}$, on the order of nanoseconds. Initially, when the interface is sharp, the donor intensity decay is single exponential (ignoring the small contribution due to NRET near the interface), while for a completely mixed case it will be similar to eq 5, with γ calculated using the average acceptor concentration across the sandwich.

In deriving eq 9 we have assumed that there is no donor–donor energy transfer and that the initial NRET before diffusion takes place is negligible. Donor–donor energy transfer is characterized by its own critical transfer distance, $R_{0\mathrm{DD}}$, which is normally much smaller than that for donor–acceptor transfer (e.g., the values of critical transfer distance for phenanthrene–phenanthrene and phenanthrene–anthracene are $R_{0\mathrm{DD}} \approx 0.88$ nm and $R_{0\mathrm{AD}} \approx 2.2$ nm, respectively[32]), resulting in donor–donor transfer typically being roughly an order of magnitude or more less likely than donor–acceptor transfer at equal donor–donor and donor–acceptor separation distances. A method for limiting donor–donor transfer is to use an initial donor concentration which is less than that of the acceptor.

While it is theoretically possible to determine diffusion coefficients by measuring the donor fluorescence intensity decay for samples annealed for various diffusion times and fitting those curves to eq 9 presuming a certain diffusion coefficient (which in turns yields $C_{\mathrm{DN}}(z,t)$), in practice this would be a particularly burdensome approach. Instead, it is convenient to determine the efficiency of energy transfer, $E(t)$,[40] using the following equation:

$$E(t) = 1 - \int_0^{\infty} I_{\mathrm{DN}}(\bar{t}/\tau_{\mathrm{d}},t)\,\mathrm{d}(\bar{t}/\tau_{\mathrm{d}}) \quad (10)$$

where I_{DN} is given by eq 9. The integral in eq 10 merely represents the area under the donor fluorescence intensity decay curve at a given annealing time normalized to that area obtained at zero annealing time. Therefore, $E(t) = 0$ prior to annealing; it will always be bound by a value less than 1 which depends on initial acceptor concentration. Using eqs 9 and 10, we have

$$E(t) = 1 - \left[\frac{1}{x}\int_0^{x+y} C_{\mathrm{DN}}(z,t) \times \int_0^{\infty}\exp\left(-\frac{\bar{t}}{\tau_{\mathrm{d}}} - 2\gamma(z,t)\left(\frac{\bar{t}}{\tau_{\mathrm{d}}}\right)^{1/2}\right)\mathrm{d}(\bar{t}/\tau_{\mathrm{d}})\,\mathrm{d}z\right] \quad (11)$$

The integration with decay time can be written as[38,39]

$$\int_0^{\infty}\exp\left(-\frac{\bar{t}}{\tau_{\mathrm{d}}} - 2\gamma\left(\frac{\bar{t}}{\tau_{\mathrm{d}}}\right)^{1/2}\right)\mathrm{d}(\bar{t}/\tau_{\mathrm{d}}) = 1 - \pi^{1/2}\gamma\exp(\gamma^2)[1 - \mathrm{erf}(\gamma)] \quad (12)$$

Therefore, eq 11 may be simplified to

$$E(t) = 1 - \left[\frac{1}{x}\int_0^{x+y} C_{\mathrm{DN}}\{1 - \pi^{1/2}\gamma\exp(\gamma^2)[1 - \mathrm{erf}(\gamma)]\}\mathrm{d}z\right] \quad (13)$$

An analytical solution of eq 13 using the concentration profiles given by eqs 7a and 7b is complicated. However, for $t < x^2/(16D_{\mathrm{p}})$, we can use eqs 7b and 8 to obtain

$$E(t) = \frac{(D_{\mathrm{p}}t)^{1/2}}{x} \times \left\{\int_{-x/2(D_{\mathrm{p}}t)^{1/2}}^{y/2(D_{\mathrm{p}}t)^{1/2}} [1 - \mathrm{erf}(s)]\{\pi^{1/2}a\exp(a^2)[1 - \mathrm{erf}(a)]\}\,\mathrm{d}s\right\} = \frac{(D_{\mathrm{p}}t)^{1/2}}{x}\{k\} \quad (14)$$

where $s = (z - x)/(2(D_{\mathrm{p}}t)^{1/2})$ and

$$a(s) = \frac{C_{\mathrm{A0}}}{2A_0}[1 + \mathrm{erf}(s)] \quad (15)$$

The term in braces in eq 14, k, is a function of C_{A0}/A_0. Figure 2 shows the dependence of k on C_{A0}/A_0. Employing $R_{0\mathrm{AD}} = 2$ nm, we find that $A_0 = 0.06$ mol/L; given that it is unlikely that any experiment employing end-labeled polymers will have C_{A0}/A_0 exceeding 1, k should not exceed 0.911. (For systems which are randomly labeled rather than end-labeled, C_{A0}/A_0 may exceed 1.)

For the completely mixed case we have

$$E(t = \infty) = \left\{\pi^{1/2}\left[(1 - q)\frac{C_{\mathrm{A0}}}{A_0}\right]\exp\left[(1 - q)^2\left(\frac{C_{\mathrm{A0}}}{A_0}\right)^2\right] \times \left[1 - \mathrm{erf}\left((1 - q)\frac{C_{\mathrm{A0}}}{A_0}\right)\right]\right\} \quad (16)$$

The normalized efficiency of energy transfer, $E_{\mathrm{N}}(t)$, can be written as

$$E_{\mathrm{N}}(t) = \frac{E(t)}{E(t \cong \infty)} = k_{\mathrm{n}}\left(\frac{(D_{\mathrm{p}}t)^{1/2}}{x}\right) \quad (17)$$

(Later we will show that $E_{\mathrm{N}}(t)$ is equal to $I_{\mathrm{AN}}(t)$, the normalized steady-state acceptor fluorescence intensity.) Figure 3 shows the dependence of k_{n} (for $q = {}^1/_2$ or $x = y$) as a function of C_{A0}/A_0. It is important to note that the value of k_{n} is equal to 1.60 for small values of C_{A0}/A_0. However, for higher values of C_{A0}/A_0, k_{n} is not a constant. For the specific case of $C_{\mathrm{A0}} = A_0$ and $x = y$, we can write the efficiency, $E(t)$, and the normalized efficiency, $E_{\mathrm{N}}(t)$, as follows:

$$E(t) = (0.911)[(D_{\mathrm{p}}t)^{1/2}/x] \quad (18)$$

$$E_{\mathrm{N}}(t) = (1.67)\left[\frac{(D_{\mathrm{p}}t)^{1/2}}{x}\right] \quad (19)$$

For $t > x^2/(16D_{\mathrm{p}})$ the solutions for $E(t)$ and $E_{\mathrm{N}}(t)$ can be obtained numerically.

In order to demonstrate the sensitivity of the NRET method just described, Figure 4 illustrates the dependence of $I_{\mathrm{DN}}(\bar{t},t)$ (determined using eqs 7 and 9) on $(D_{\mathrm{p}}t)^{1/2}/x$ for $C_{\mathrm{A0}} = A_0$ and $x = y$. Also included in Figure 4 is the donor

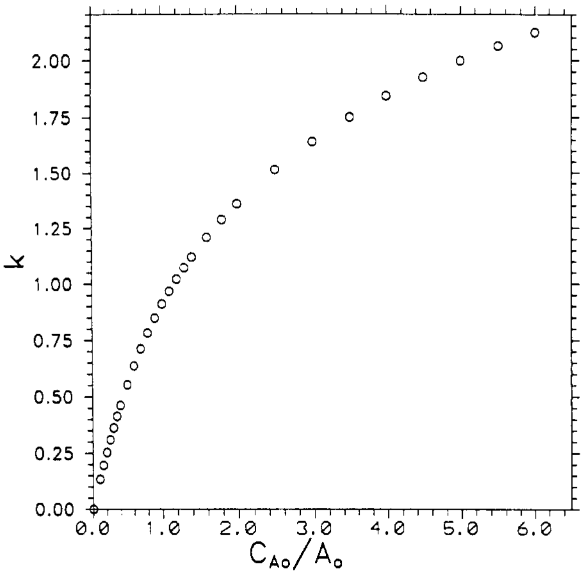

Figure 2. Values of k, the term in parentheses in eq 14, as a function of C_{A0}/A_0 (for $x = y$).

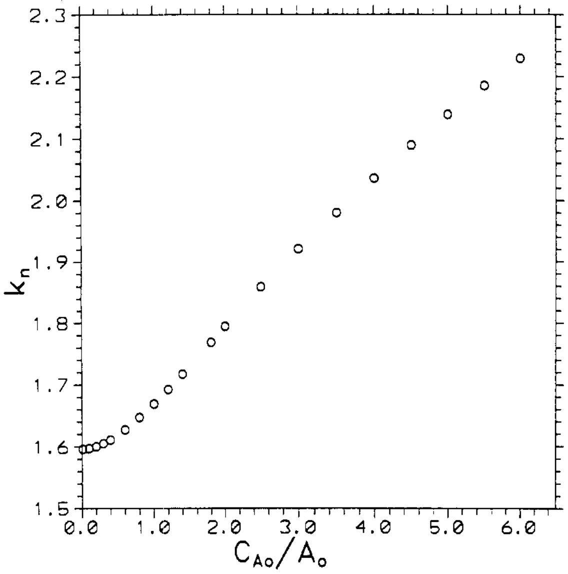

Figure 3. Values of k_n, the term in parentheses in eq 17, as a function of C_{A0}/A_0 (for $x = y$).

intensity decay for the fully mixed case when $C_A = A_0/2$ and $C_{DN} = 0.5$. These results indicate that the donor fluorescence intensity decay provides excellent sensitivity for determining D_p within a small range of error. The values of $E(t)$ and $E_N(t)$ (for $C_{A0} = A_0$ and $x = y$) are shown in Figure 5. The values of $E(t)$ and $E_N(t)$ for $t < x^2/(16D_p)$ were determined using eqs 18 and 19 and for $t > x^2/(16D_p)$ were determined numerically using eqs 7 and 13. Noteworthy is the absolute change in the efficiency between the unmixed and the mixed case; e.g., if the donor chromophore has an excited-state lifetime of 40 ns in the absence of acceptors, then on complete mixing (for $C_{A0} = A_0$ and $x = y$) the apparent average excited-state lifetime will reduce to around 18 ns.

If instrumentation to evaluate the donor intensity decay is not available, D_p may also be determined by steady-state fluorescence measurements. In that case the sample is illuminated at an excitation wavelength preferentially absorbed by the donor, and either the steady-state acceptor fluorescence intensity, $I_A(t)$, or donor fluorescence intensity, $I_D(t)$, may be monitored as a function of diffusion time. Depending on the photostability of the donor and acceptor chromophores at elevated temperatures, these measurements may be made in situ with fluorescence monitored during the diffusion process or by off-line measurements with diffusion occurring in an environmental chamber and fluorescence intensity measured at a lower temperature after removal of the sample from the chamber.

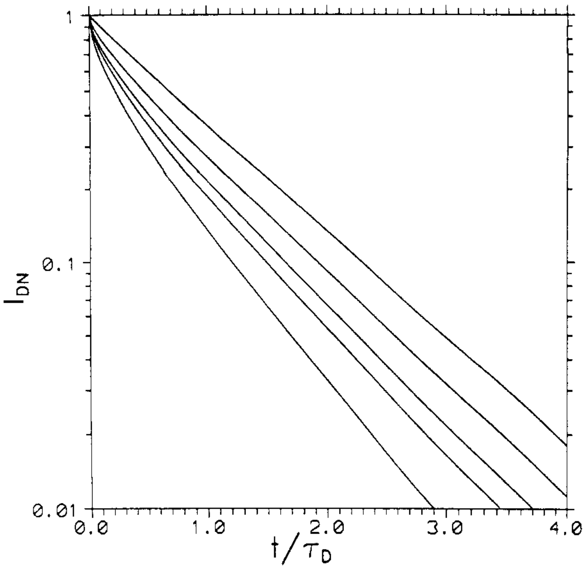

Figure 4. Normalized donor intensity decay, $I_{DN}(\bar{t}/\tau_d, t)$, for interdiffusion of acceptor- and donor-labeled polymer. From top to bottom, $(D_p t)^{1/2}/x = 0.0, 0.25, 0.40,$ and 0.50. These profiles were obtained by numerical integration of eq 9 using $C_{A0} = A_0$, $x = y$, and the concentration profiles given by eqs 7a and 7b. Also shown is the donor intensity decay for the completely mixed case ($t \approx \infty$) when $\gamma = 0.5$ and $C_{DN} = 0.5$ everywhere in the sample.

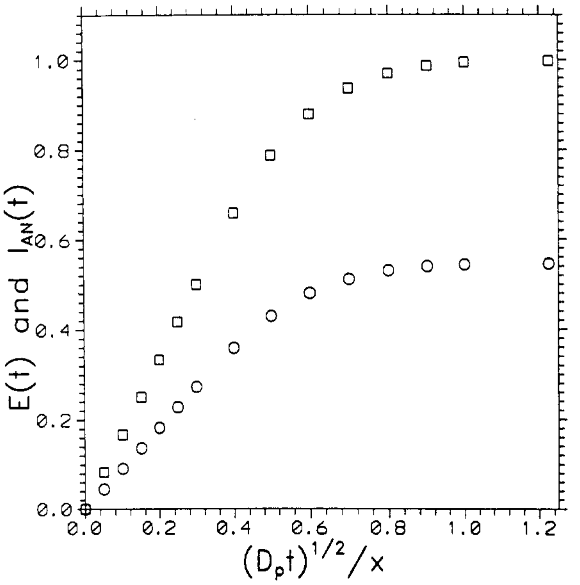

Figure 5. Values of $E(t)$ (○) and $I_{AN}(t)$ (□) as a function of $(D_p t)^{1/2}/x$ (for $C_{A0} = A_0$ and $x = y$). (Note: $I_{AN}(t) = E_N(t)$.)

The increase in $I_A(t)$ or decrease in $I_D(t)$ beyond the value at zero time is simply due to the increase in energy-transfer efficiency. A normalized steady-state acceptor intensity, $I_{AN}(t)$, for $t < x^2/(16D_p)$ may be defined as follows:

$$I_{AN}(t) = \frac{I_A(t) - I_A(t=0)}{I_A(t \cong \infty) - I_A(t=0)} = E_N(t) = k_n \frac{(D_p t)^{1/2}}{x} \quad (20)$$

where k_n is the same as in eq 17. (For $t > x^2/(16D_p)$ the value of $I_{AN}(t)$ has to be obtained numerically.) This definition of $I_{AN}(t)$ allows one to account only for the increase in acceptor intensity associated with energy transfer and thus is equivalent to $E_N(t)$. Similarly for $t < x^2/(16D_pt)$, the decrease in the normalized steady-state donor intensity, $I_{DN}(t)$, can be written as

$$I_{DN}(t) = \frac{I_D(t) - I_D(t \cong \infty)}{I_D(t=0) - I_D(t \cong \infty)} = 1 - E_N(t) = 1 - k_n \frac{(D_pt)^{1/2}}{x} \tag{21}$$

Thus, the increase in the steady-state acceptor intensity and the decrease in donor intensity are related to the measurement of both the energy-transfer efficiency calculable from transient donor fluorescence intensity decay measurements and the polymer self-diffusion coefficient.

(B) Comparison with Previous Approaches To Interpret NRET Data. The general formalism described in section A above provides quantitative methods to determine the polymer self-diffusion coefficient, D_p, using both steady-state acceptor (or donor) fluorescence intensity and transient donor fluorescence decay measurements. The transient donor fluorescence intensity decay measurements can be interpreted using eq 17, provided $t < x^2/(16D_pt)$. (For longer times, eq 17 does not provide an exact solution, but solutions can be obtained via numerical simulations.) Several identical polymer sandwiches can be annealed for various times at a temperature of interest. Then each sample can be analyzed ex situ using a transient fluorescence decay apparatus. The areas under the decay curves can be used to determine $E_N(t)$, and the resulting values of $E_N(t)$ should be linear in $t^{1/2}$ with a slope of $k_nD_p^{1/2}/x$. Similarly, the steady-state acceptor and donor fluorescence intensity measurements can be interpreted using eqs 20 and 21, respectively, with $I_{AN}(t)$ showing an increase which is linear in $t^{1/2}$ with a slope of $k_nD_p^{1/2}/x$ and $I_{DN}(t)$ showing a decrease linear in $t^{1/2}$ with a slope of $-k_nD_p^{1/2}/x$. Measurements may be made in either an in situ or an ex situ mode, depending on conditions of photostability of the chromophores at the annealing temperatures of interest. (In all cases, care must be taken to minimize the effects of scattered light contaminating the observed fluorescence intensity or intensity decay and, in the case of steady-state intensity measurements, to ensure that film thicknesses and chromophore concentrations are low enough that radiative energy-transfer effects are negligible. Otherwise, incorrect characterization of the energy-transfer efficiency and diffusion coefficients is possible.)

Equation 20 bears significant resemblance to results obtainable using eq 1 from the approach proposed by Tirrell, Adolf, and Prager.[18] They proposed the use of eq 1 for interdiffusion of lightly labeled, identical polymers with $C_{A0} = C_{D0}$. For $t < x^2/(16D_p)$ and $x = y$, we can recast eq 1 using Fickian concentration profiles:

$$I_A(t) = \frac{C_{A0}C_{D0}I_0\alpha}{4}\int_0^{x+y}\left[1 - \operatorname{erf}\left(\frac{z-x}{2(D_pt)^{1/2}}\right)\right] \times \left[1 + \operatorname{erf}\left(\frac{z-x}{2(D_pt)^{1/2}}\right)\right] \mathrm{d}z \tag{22}$$

Equation 22 can be solved analytically to give

$$I_{AN}(t) = \frac{I_A(t) - I_A(0)}{I_A(t \cong \infty) - I_A(0)} = (1.60)\frac{(D_pt)^{1/2}}{x} \tag{23}$$

Thus, the Tirrell–Adolf–Prager picture indicates that, in agreement with eq 20, $I_{AN}(t)$ is proportional to $(D_pt)^{1/2}/x$. In contrast to eq 20, the proportionality in eq 23 is a constant rather than a function of C_{A0}/A_0. However, as shown from Figure 3, in the limit $C_{A0}/A_0 \leq 0.4$, $k_n = 1.60$ and eq 23 is valid. Thus, the Tirrell–Adolf–Prager picture is demonstrated to be a limiting case of the formalism described here. The present formalism allows for higher acceptor concentrations which may be useful to optimize NRET conditions.

In contrast to the comparison with the Tirrell–Adolf–Prager approach, the picture proposed by Winnik and co-workers[19] does not prove to be a limiting case of the general formalism outlined to section A above. Winnik and co-workers have used eq 2 as a means to monitor interdiffusion of acceptor- and donor-labeled polymers in latex particles. As a simplified analysis, they assumed that the donor intensity decay may be taken as being due to two distinct regions, one region that consists of donor chromophores in the absence of acceptors and the second where the donor chromophores are mixed with the acceptors in the absence of a concentration gradient of acceptors. By employing this approach, Winnik and co-workers were the first to demonstrate the utility of fluorescence decay measurements in following and quantifying interdiffusion in polymeric systems. (Such an approach has the advantage of removing the effects of any radiative energy transfer which may "contaminate" the steady-state fluorescence intensity as fluorescence lifetimes are unaffected by radiative energy-transfer effects.) Winnik and co-workers themselves pointed out that this approach was only approximate in allowing for quantification of diffusion coefficients. Recently, they have initiated studies[51] to recover acceptor concentration distributions from analysis of intensity decay measurements in interdiffusion experiments. We should note that the success of Winnik's experimental approach for following interdiffusion in part inspired this study in which a more exact quantitative relationship between energy transfer and diffusion has been determined.

In order to demonstrate the quantitative differences in calculating diffusion coefficients using eq 2 as compared to using the formalism described in section A, let us consider the example of $C_{A0} = A_0$ and three separate values of $(D_pt)^{1/2}x$: 0.05, 0.15, and 0.25. A comparison of the donor intensity decays predicted by eqs 2 (used in ref 19) and 9 (from the general formalism described in section A) is given in Figure 6. It is clear that the decays given by eq 2 are in disparity with those given by eq 9. For a given decay, the use of eq 2 would require a fit to a smaller value of the polymer self-diffusion coefficient than is the real case. This is made most clear by comparing the case of $(D_pt)^{1/2}/x = 0.25$ using eqs 2 and 9. According to the simplified model by Winnik and co-workers,[19] this corresponds to $B_1 = 1.0$ with complete mixing, no concentration gradient in donors or acceptors. Using the formalism presented here, this state of mixing is approximately achievable only for $(D_pt)^{1/2}/x \geq 0.8$. Consequently, according to the formalism developed in section A (see Figure 5), this would mean that the simplified approach would underestimate the effective polymer self-diffusion coefficient by at least a factor of 10. In the case of $(D_pt)^{1/2}/x = 0.15$, the simplified approach predicts a value of D_p which is approximately 5–6 times smaller than the one obtained using the general formalism detailed in section A.

Recently, as a substitute for using eq 2 Winnik and co-workers[19d,f] have proposed the use of the area under the normalized intensity decay curve to determine the volume fraction of mixing, f_m:

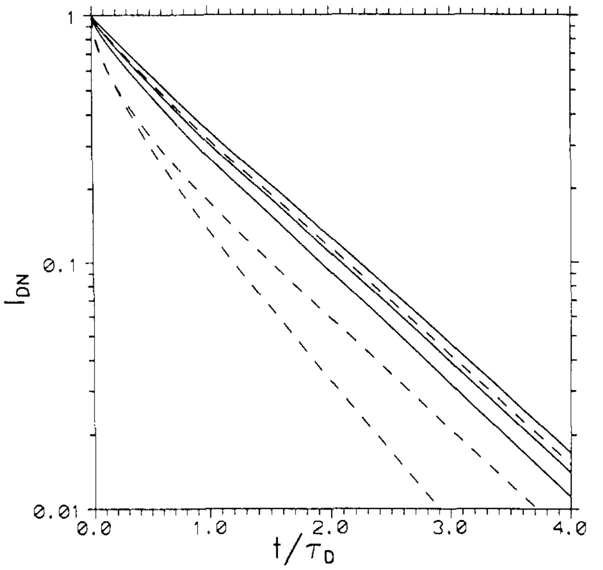

Figure 6. Normalized donor intensity decays using eq 2 (dashed curves) and eq 9 (solid curves) for the conditions $C_{A0} = A_0$ and $x = y$. From top to bottom, $(D_pt)^{1/2}/x = 0.05$ (which for the dashed curve corresponds to $B_1 = 0.20$), 0.15 (which for the dashed curve corresponds to $B_1 = 0.40$), and 0.25 (which for the dashed curve corresponds to $B_1 = 1.0$).

$$f_m = B_1 = \frac{\int_0^\infty I_{DN}(t,\bar{t})\,d\bar{t} - \int_0^\infty I_{DN}(0,\bar{t})\,d\bar{t}}{\int_0^\infty I_{DN}(\infty,\bar{t})\,d\bar{t} - \int_0^\infty I_{DN}(0,\bar{t})\,d\bar{t}} \qquad (24)$$

It is important to note that the right-hand side of eq 24 is our definition of $E_N(t)$. By relating the volume fraction of mixing to $E_N(t)$, Winnik and co-workers have made the assumption that eq 2 is valid, with γ being a constant. We have already shown that ignoring the acceptor and donor concentration gradients in the mixed region leads to errors. Although the approaches used by Winnik and co-workers for quantifying diffusion coefficients from fluorescence intensity decays are inexact, their experiments and analyses have proven very important in demonstrating the utility of fluorescence decay measurements in studying diffusion in polymeric systems. The analysis provided by the formalism given in section A allows for more exact quantitative determinations of diffusion coefficients to result from those measurements.

It should be noted that, in contrast to the sandwich-like, one-dimensional diffusion problem addressed here, Winnik's studies[19] on polymer latexes specifically employ a spherical diffusion model for analysis of their data in which a donor-labeled polymer sphere is surrounded by a sea of acceptor-labeled polymer molecules. In a forthcoming study,[52] it will be demonstrated that the degree of error in estimating diffusion coefficients resulting from using eq 2 or 24 is not a consequence of the experimental geometry but is a result of approximating the intermixed region as having a constant acceptor concentration equivalent to the average in that region.

Conclusions

NRET provides a relatively inexpensive way to characterize quantitatively self-diffusion coefficients of polymers above T_g. When two identical polymer films, one labeled with fluorescence donors and the other with acceptors are brought into contact above T_g, interdiffusion of chains occurs with time. This results in an increase in both the normalized steady-state acceptor intensity, $I_{AN}(t)$, and the normalized efficiency of energy transfer, $E_N(t)$. In this paper, a general formalism is provided to relate quantitatively $I_{AN}(t)$ and $E_N(t)$, to the polymer self-diffusion coefficient, D_p. In the limit of Fickian diffusion and $t < x^2/(16D_p)$, where x is the thickness of the donor-labeled polymer film, both $I_{AN}(t)$ and $E_N(t)$ are equal to $k_n(D_pt)^{1/2}/x$, where the factor k_n is a function of the initial acceptor concentration. For $t > x^2/(16D_p)$ the values of $I_{AN}(t)$ and $E_N(t)$ need to be obtained numerically.

The Tirrell–Adolf–Prager[18] approach for interpreting the increase in steady-state acceptor intensity is shown to be a limiting case of the present formalism, relevant at low acceptor concentration. In contrast, the picture proposed by Winnik and co-workers[19] for interpreting donor fluorescence intensity decay measurements does not prove to be a limiting case of the general formalism presented here. By combining Winnik's experimental approach, which is the first to demonstrate how fluorescence intensity decay measurements can be used to estimate interdiffusion coefficients in polymer systems, with the analysis provided in this study, which adequately accounts for the concentration gradients of donor and acceptor chromophores, more exact quantitative determinations of polymer diffusion coefficients are possible.

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